

Quantum Chemical Studies for the Structure-Property Relationships of the Fluoro-isothiocyanated Nematic Liquid Crystal Materials

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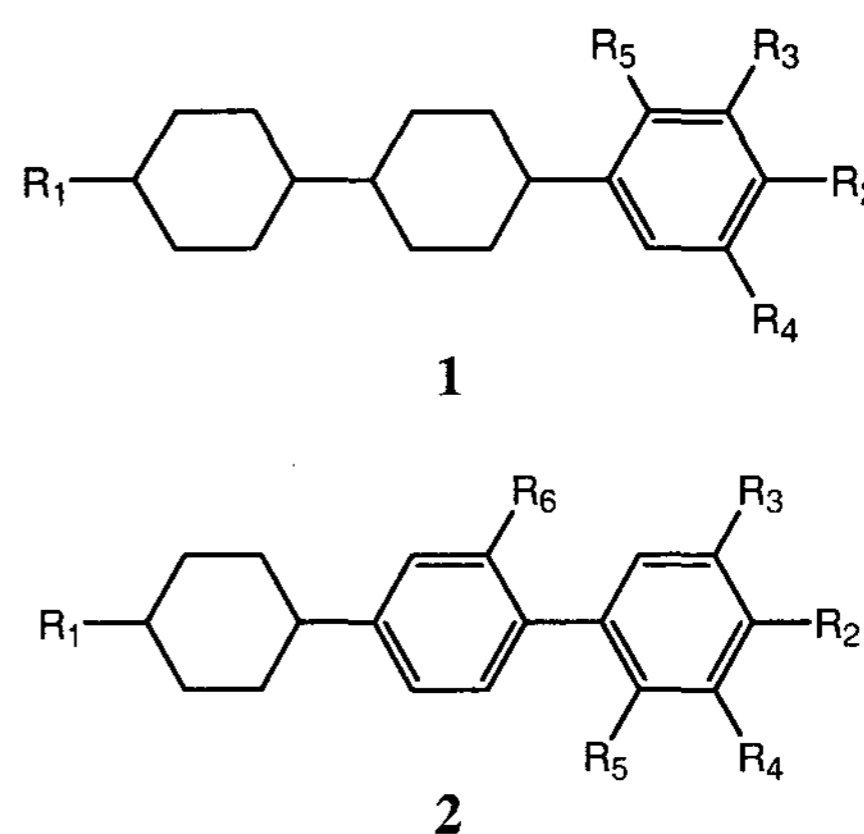
Abstract

Some important properties of the liquid crystal molecules containing fluoro-isothiocyanated molecules have been studied using quantum chemical calculations and the results were correlated with respect to the structure of the molecules. Dielectric anisotropy, birefringence have been predicted for several unknown structures. The Maier-Meier, Vuks equation were used for the dielectric anisotropy and birefringence calculation. The results obtained by empirical approximation showed a good agreement with experiment ones.

1. Introduction

The use of liquid crystals in the particular applications, such as electro-optical display, requires optimization of several physical properties. These properties include dielectric constants, refractive indices, viscosity, and elastic constants. However, the most basic requirement is that the liquid crystalline phase must exist in an appropriate temperature range for the desired applications. Many experimental and theoretical studies have been reported for these properties. Recently, some calculation results for the dielectric anisotropy and birefringence showed a good agreement with experimental results [1-3]. Tarumi et. al reported dielectric anisotropy and birefringence of the molecules with F, OCF₃, CF₃, CN group from the molecular dipole moments and polarizabilities using AM1 method. The calculated values are in good agreement with the experimental results for some

compounds containing different core structures and substituents. In this paper we have studied the properties of newly synthesized phenyl bicyclohexyl compounds with thiocyanide group on phenyl ring. The structures depicted in 1 and 2 were optimized by AM1 method and then dipole moments, and polarizabilities of the molecules were refined by DFT method. The calculation results were correlated with experimental results to investigate the statistical methodology for understanding the physical, optical properties of LC materials.



2. Method

The AM1 of MOPAC 6.0 and DFT(Density Functional Theory), B3LYP 6-31G* of Gaussian 98 [4] program were used for the optimization of the molecular structures and their physical properties such

as dipoles and polarizabilities. The dielectric anisotropy, $\Delta\epsilon$ is the difference between the dielectric permittivities, parallel (ϵ_{\parallel}) and perpendicular (ϵ_{\perp}) to the director. It can be calculated by the Maier-Meier equation (1) [5].

$$\Delta\epsilon = \frac{NFh}{\epsilon_0} \left\{ \Delta\alpha - \frac{F\mu^2}{2k_B T} (1 - 3\cos^2\beta) \right\} S \quad (1)$$

where N is the number of molecules per unit volume, k_B the Boltzmann constant, and T the temperature for measurement. β has been obtained from optimized structure by AM1 calculation measuring the angle between the molecular dipole moment and the long axis of the molecule. Order parameter, S was quoted from Xu's report which is estimated by the following equation [3]:

$$S = S_0(1 - T/T_{NI})^{\gamma} \quad (2)$$

3. Results and discussion

The dielectric anisotropies of the molecules was calculated using the Maier-Meier equation [5] and the birefringences using the Vuk's equation [6]

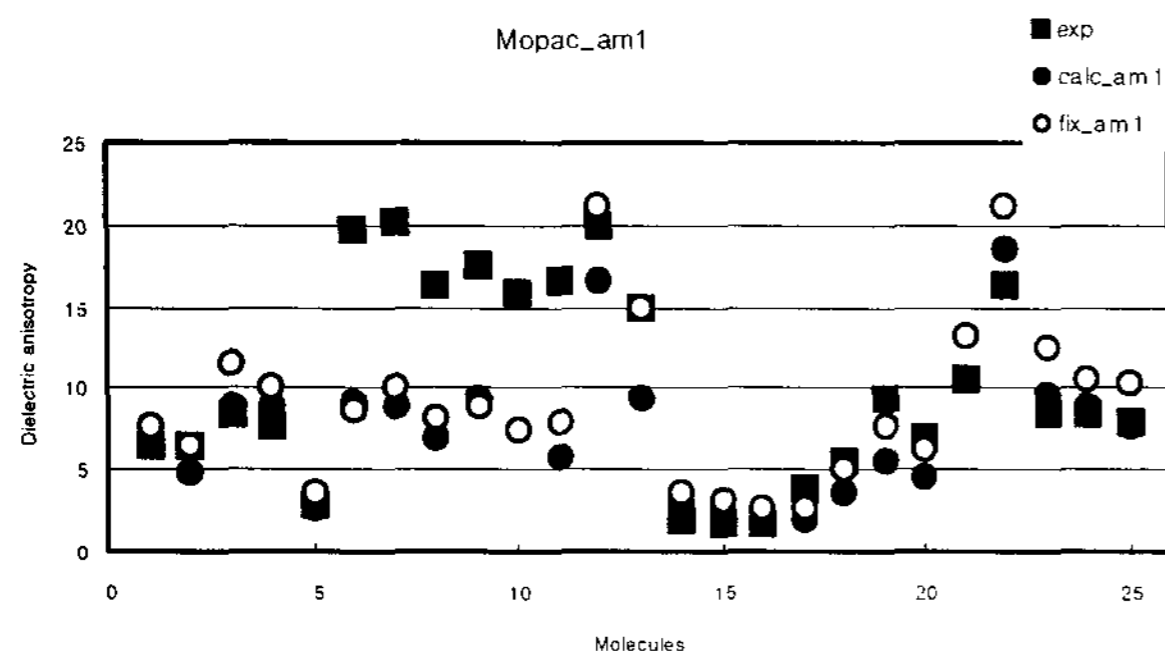


Figure 1. Comparison of the experimental and the calculated results for dielectric anisotropy of the molecules.

The dielectric anisotropies and the birefringences of the compounds with F, CF_3 , OCF_3 , CN showed a good agreement with experimental results however those with NCS showed large discrepancies. The deviation of calculated $\Delta\epsilon$ from the experimental values were

around 2.59.

Correlation coefficient (r^2) for dielectric anisotropy (Figure 2) was 0.49 whereas that of birefringence (Figure 3) was 0.86. The compounds with F, OCF_3 , CF_3 , CN group showed a good agreement with experimental results however those of molecules with NCS group showed lot of disagreement with experiment.

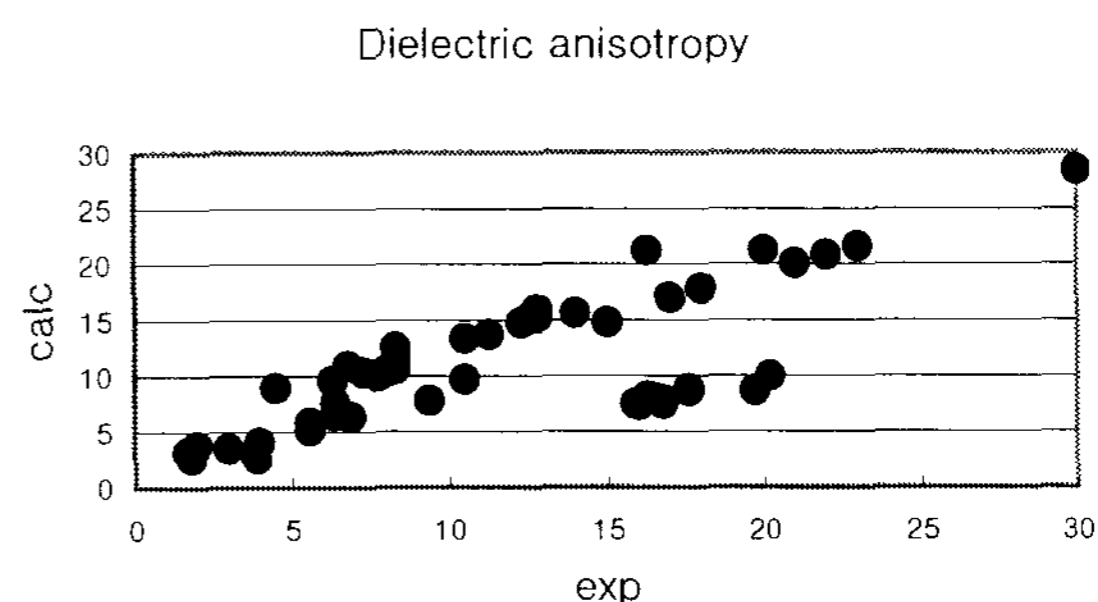


Figure 2. Least square fit of experimental measurements and calculation results for dielectric anisotropy ($\Delta\epsilon$).

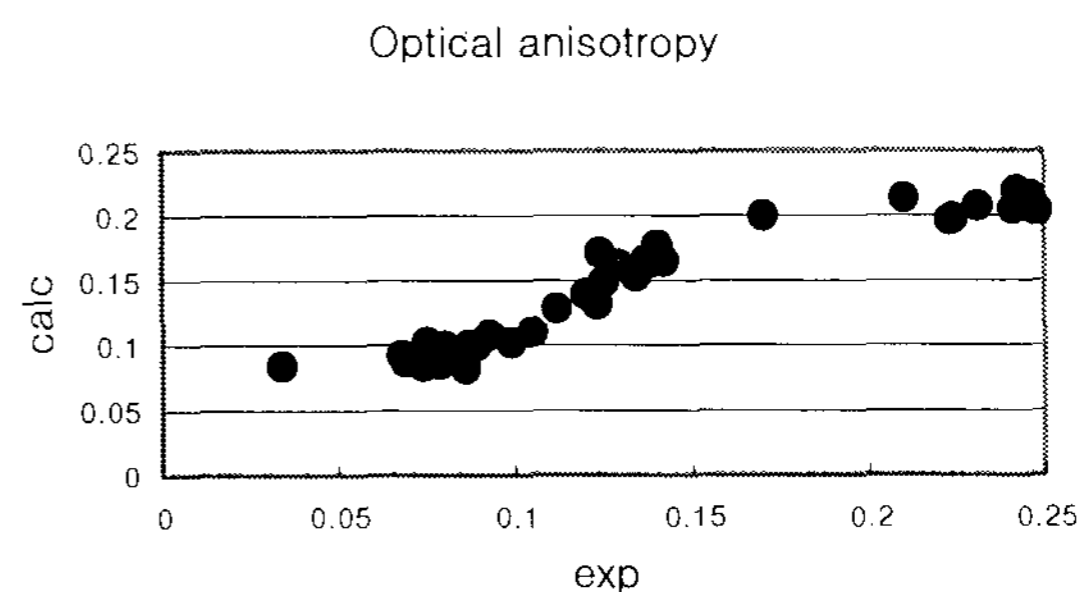


Figure 3. Least square fit of experimental measurements and calculation results for birefringence (Δn).

For the improvement of large discrepancy of the NCS substituted molecule, density functional calculations (DFT) were performed. The average deviation from the experimental results of $\Delta\epsilon$ for thio-cyanated (NCS) molecules improved significantly. The $\Delta\epsilon$ obtained using dipole moment and polarizability calculated by B3LYP/6-31G* method was 4.71 whereas that from AM1 calculations results 7.19. The

birefringence, Δn of thiocyanated molecules, 0.029 was improved to 0.002 using the B3LYP/6-31G* method. Correlations between the calculations and the experimental measurements are given in Figure 3. The improved correlation coefficient (r^2) of dielectric anisotropy for thiocyanated molecules was 0.89 (empty circles) after application of correction factor 0.78 to the theoretical results (dark circles) (Figure 4).

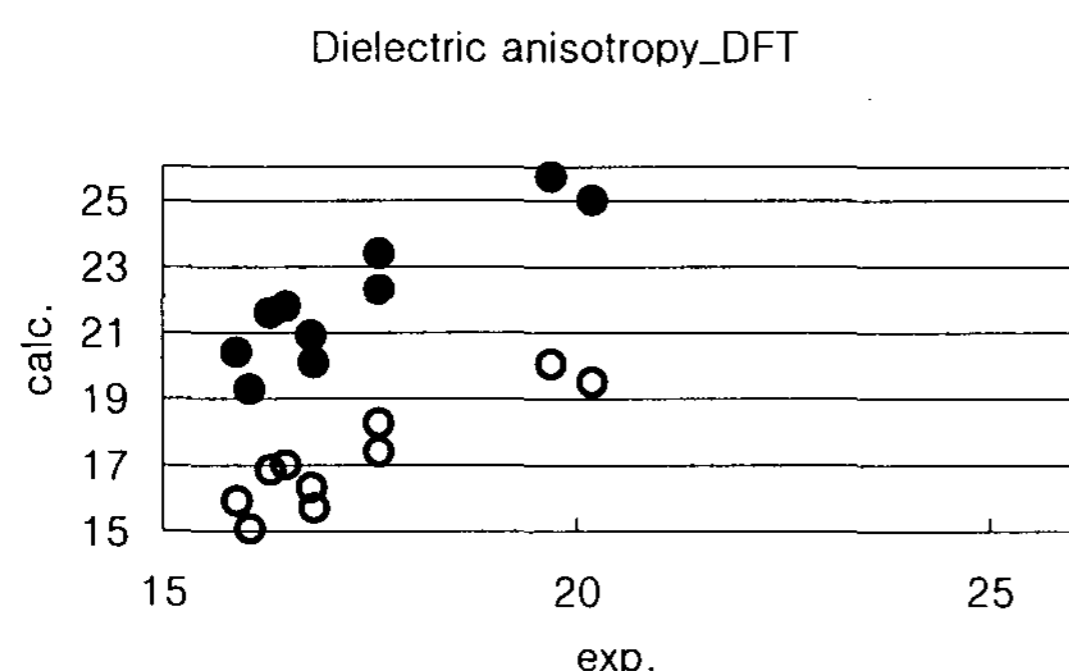


Figure 4. Least square fit of experimental measurements and calculation results for birefringence($\Delta \epsilon$) of NCS substituted molecules. Empty circles ($r^2=0.89$) represent the correlations after application of factor 0.78 to the calculation results dark circle.

The reason for large discrepancy of NCS substituted molecules is considered to be derived from the errors in polarizability anisotropy ($\Delta\alpha$) and dipoles (μ) values. Semi-empirical AM1 method underestimated the $\Delta\alpha$ and μ giving smaller values compared to the experimental measurements. The ab-initio, DFT method gave the $\Delta\alpha$ about twice larger than those obtained by AM1 method.

4. Conclusion

The conformational studies for the LC molecules revealed the reasons behind the discrepancies of the calculation results and high level DFT calculation improved the accuracy of the results. The correlation coefficient (r^2) of dielectric anisotropy for thiocyanated molecules was improved up to 0.89. It is expected that the results combined with statistical methods can be utilized for the prediction of the physical optical properties of the LC materials.

5. Acknowledgements

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6. References

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